

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 814 097 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication  
29.12.1997 Bulletin 1997/52

(51) Int Cl<sup>6</sup> **C08F 4/00, C08F 293/00,  
C08F 291/00**

(21) Application number **97303948.0**

(22) Date of filing **06.06.1997**

(84) Designated Contracting States  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**

(30) Priority **17.06.1996 US 664702**

(71) Applicant **XEROX CORPORATION  
Rochester New York 14644 (US)**

(72) Inventors  
• **Kazmaier, Peter M.**  
**Mississauga, Ontario L5L 1E5 (CA)**  
• **Keoshkerian, Barkev**  
**Thornhill, Ontario L4J 7E8 (CA)**

• **Moffat, Karen A.**  
**Brantford, Ontario N3P 1N2 (CA)**  
• **Georges, Michael K.**  
**Guelph, Ontario N1G 3N8 (CA)**  
• **Hamer, Gordon K.**  
**Mississauga, Ontario L5L 2P4 (CA)**  
• **Veregin, Richard P.N.**  
**Mississauga, Ontario L5L 5C3 (CA)**

(74) Representative **Pike, Christopher Gerard et al**  
**Rank Xerox Ltd.,**  
**Patent Department,**  
**Parkway**  
**Marlow, Buckinghamshire SL7 1YL (GB)**

(54) **Processes for preparing telechelic, branched and star thermoplastic resin polymers**

(57) A process for the preparation of branched thermoplastic resins comprising heating a mixture of a free radical initiator, at least one first free radical reactive monomer, at least one free radical reactive branching agent compound, and at least one stable free radical agent to produce a linear or unbranched polymer product with a free radical initiator fragment at one end and

a covalently bonded stable free radical agent at the other end of the polymerized chain of monomers, and irradiating the unbranched polymer product in the presence of a reactive compound selected from the group consisting of a free radical reactive monomer, a branching agent compound, and mixtures thereof to form a branched polymeric product.

EP 0 814 097 A2

## Description

The present invention is generally directed to processes for the preparation of branched or dendrimeric homopolymers and copolymers. More specifically, the present invention relates to improved polymerization processes which provide branched, star and dendrimeric homopolymer and copolymer resin products which possess narrow polydispersity properties and which polymerization processes proceed with high monomer to polymer conversion. In particular, this invention relates to stable free radical mediated pseudoliving polymerization processes which yield branched homopolymers and copolymers having number average molecular weights ( $M_n$ ) above about 100 to about 200,000 and having a polydispersity ratio of the weight average molecular weight ( $M_w$ ) to the number average molecular weight ( $M_n$ ) of from about 1.0 to about 2.0 and which processes accomplished in accordance with the present invention provide numerous operational and economic advantages.

Many polymerization processes used for the synthesis of narrow polydispersity resins, such as anionic, cationic, and group transfer polymerization processes, are severely limited by the need for anhydrous reaction conditions and monomers which do not contain protic or reactive functional groups, for example, hydroxy (OH), carboxy ( $\text{CO}_2\text{H}$ ), amino (NH) and the like. As a consequence, these processes are not readily applicable to the polymerization of functionalized monomers since these monomer materials tend to be hygroscopic and any associated water may readily destroy the polymerization initiator component, for example, the hydrolysis or protonation of organolithium reagents by the monomer in anionic polymerization processes, or in other ways cause the polymerization to fail entirely or to be industrially inefficient.

Of the known polymerization processes a preferred way to prepare branched or dendrimer polymers or copolymers having a narrow molecular weight distribution or polydispersity is by anionic processes. The use and availability of branched or star type resins having narrow polydispersities in industrial applications is limited because anionic polymerization processes must be performed in the absence of atmospheric oxygen and moisture, require difficult to handle and hazardous initiator reagents, and consequently such polymerization processes are generally limited to small batch reactors. In addition, the monomers and solvents that are used must be of high purity and anhydrous thereby rendering the anionic process more expensive than alternatives which do not have these requirements. Thus, anionic polymerization processes for the preparation of branched or star type polymers are difficult and costly.

It is desirable to have free radical polymerization process that provides narrow molecular weight distribution branched or star type polymers and resins that overcomes the shortcomings and disadvantages of the aforementioned related anionic branching polymerization processes.

Similarly, group transfer polymerization (GTP) processes have limitations and disadvantages, such as anhydrous reaction conditions and expensive reagents, which disadvantage GTP processes particularly for large scale industrial preparation of branched or star polymers.

Free radical polymerization processes are generally chemically less sensitive than anionic processes to impurities in the monomers or solvents typically used and are substantially or completely insensitive to water. Conventional free radical polymerization processes that are used to polymerize monomers in general, and functionalized monomers in particular, inherently give broad polydispersity resin products or require that sophisticated processing conditions and materials handling protocols be employed.

Star polymers or dendrimers can be constructed with, for example, a rod-like tertiary structure or a spherical tertiary structure. The branching associated with these systems provide a number of unusual properties. For example, in contrast to linear polymers, the viscosity of spherical star polymers decrease as the molecular weight increases. Furthermore, compounding hydrocarbon dendrimers in a variety of media imparts increased strength to these materials.

Branched copolymers prepared by conventional free radical polymerization processes inherently have broad molecular weight distributions or polydispersities, generally greater than about four. One reason is that most free radical initiators selected have half lives that are relatively long, from several minutes to many hours, and thus the polymeric chains are not all initiated at the same time and which initiators provide growing chains of various lengths at any time during the polymerization process. Another reason is that the propagating chains in a free radical process can react with each other in processes known as coupling and disproportionation, both of which are chain terminating and polydispersity broadening reaction processes. In doing so, chains of varying lengths are terminated at different times during the reaction process which results in branched resins comprised of polymeric chains which vary widely in length from very small to very large and thus have broad polydispersities. If a free radical polymerization process is to be enabled for producing branched, dendrimeric, or star polymers with narrow molecular weight distributions, then all polymer chains and branches or arms must be initiated at about the same time and premature termination by coupling or disproportionation processes must be avoided or eliminated.

Practitioners in the art have long sought an inexpensive, efficient and environmentally efficacious means for producing branched polymers having operator controllable or selectable molecular weight and branching properties, and further, processes which selectively afford a wide variety of different polymer product types and have narrow molecular weight distribution properties.

U S. Patent No. 5,473 031, discloses a process for preparing a branched polymer from a vinyl aromatic monomer comprising copolymerizing the vinyl aromatic monomer with a monomer pair wherein the monomer pair consists of two different monomers containing functionalities which are substantially nonreactive with each other under the conditions of copolymerization and heating the copolymer produced to a temperature such that the functionalities react with each other to form branches with the polymer

U S. Patent No. 5,017 458 discloses a method for producing a graft copolymer including the steps of adding to a base polymer capable of forming first radicals when irradiated with radiation an additive capable of combining with the first radicals to form second radicals stable against oxygen, the step of irradiating the base polymer containing the additive with radiation, and the step of introducing a monomer under an atmosphere free from oxygen, thereby to graft copolymerize the irradiated base polymer and the monomer

U S. Patent No. 5,334,756, discloses a process for preparing carboxylates of polyoxyalkylene siloxanes and amines, alkylpolyoxyalkylenes, polyoxyalkylene block polymers, and the like materials, comprising subjecting a primary hydroxyl group-containing polyoxyalkylene compound or alkylpolyglucoside to mild oxidation

In European Patent Publication 349 270 B1 is disclosed a pressure-sensitive adhesive composition characterized by a block copolymer represented by the general formula  $I(BAT)_n$  wherein I represents the free radical initiator portion of an iniferter of the formula  $I(T)_n$ , T represents the termination portion of the iniferter, n is an integer of at least 2, and B represents an elastic acrylic polymer block having a glass transition temperature of at least 30°C and an A-block is formed of a monomer selected from the group consisting of methyl methacrylate, polystyrylethyl methacrylate, macromer, methyl methacrylate macromer, acrylic acid, acrylonitrile, isobornyl methacrylate, N-vinyl pyrrolidone, and mixtures thereof, the weight ratio of the B-block to the A-block in the block copolymer being from 95:5 to 50:50, and 0 to 150 parts by weight tackifier per 100 parts block copolymer. Also disclosed is a method of making the pressure sensitive adhesive which relies upon mixing and exposing an iniferter of the formula  $I(T)_n$  to an energy source in the presence of a sequence of monomer charges

U S. Patent No. 4,581 429 discloses a free radical polymerization process which controls the growth of polymer chains to produce short chain or oligomeric homopolymers and copolymers including block and graft copolymers. The process employs an initiator having the formula  $(-n \text{ part}) -N-O-X$  where X is a free radical species capable of polymerizing unsaturated monomers. The molecular weights of the polymer products obtained are generally from about 2 500 to 7 000 having polydispersities generally of about 1.4 to 1.8, at low monomer to polymer conversion. The reactions typically have low conversion rates and use relatively low reaction temperatures of less than about 100 °C, and use multiple stages

In free radical polymerization reaction processes of the prior art, various significant problems exist, for example difficulties in predicting or controlling both the polydispersity and modality of the polymers produced. These polymerization processes produce polymers with high weight average molecular weights ( $M_w$ ) and low number average molecular weights ( $M_n$ ) resulting in broad polydispersities or broad molecular weight distribution ( $M_w/M_n$ ) and in some instances low conversion. Further, polymerization processes of the prior art, in particular free radical processes, are prone to generating excessive quantities of heat since the polymerization reaction is exothermic. As the viscosity of the reaction medium increases dissipation of heat becomes more difficult. This is referred to as the Trommsdorff effect as discussed and illustrated in Principles of Polymerization, G Odian, 2nd Ed., Wiley-Interscience, N.Y. 1981, page 272, the disclosure of which is entirely incorporated herein by reference. This is particularly the situation for reactions with high concentrations of soluble monomer, for example greater than 30 to 50 percent by weight soluble monomer, which are conducted in large scale reactors with limited surface area and limited heat dissipation capacity. Moreover, the exothermic nature of free radical polymerization processes is often a limitation that severely restricts the concentration of reactants or the reactor size upon scale up.

Further, gel body formation in conventional free radical polymerization processes may result in a broad molecular weight distributions and/or difficulties encountered during filtering, drying and manipulating the product resin, particularly for highly concentrated reactions.

Other problems associated with the prior art methods for preparing branched or star type dendrimeric polymeric materials is that they typically provide products with highly variable branch length, variable branch molecular weight and polydispersities, and variable particle size, for example

These and other disadvantages are avoided, or minimized with the branching polymerization processes of the present invention

These and other problems have been unexpectedly ameliorated by the present invention wherein there are provided superior results arising from polymerization or copolymerizing, for example by heating, with an initiator compound containing at least one covalently bonded stable "free radical" functional group, at least one free radical polymerizable monomer, and at least one free radical reactive branching agent to form an unbranched polymeric product containing latent or incipient branching functionality, irradiating a mixture of the aforementioned unbranched polymeric product and a second stable free radical agent to form an intermediate branched polymeric product wherein the second stable free radical agent are covalently attached to the intermediate product at sites corresponding to where the branching

agents have been integrated into the polymer and heating the resulting intermediate branched polymeric product and at least one second free radical polymerizable monomer to form a first branched polymeric product wherein the second free radical polymerizable monomer is integrated into the polymer chain at branching agent loci and as illustrated herein

According to one aspect of the present invention there is provided a process for the preparation of a thermoplastic resin or resins comprising heating a mixture comprising an initiator compound of the formula  $A \cdot T$  wherein A represents a group having at least one carbon atom and is such that a free radical  $A \cdot$  arising therefrom is capable of polymerizing an unsaturated monomer by free radical polymerization and the free radical functionality thereof resides on the at least one carbon atom, and T is a covalently bonded stable free radical compound, at least one free radical polymerizable monomer of the formula M1, and at least one free radical reactive branching agent of the formula B, to form an unbranched polymeric product of the formula  $A \cdot (M1)_m \cdot (B)_n \cdot T$  where m and n are integers from 1 to about 10,000 representing the total number of monomers M and B contained in the unbranched product, irradiating a mixture of the unbranched polymeric product and a second stable free radical compound of the formula  $T'$  to form an intermediate branched polymeric product of the formula  $A \cdot (M1)_m \cdot [B \cdot (T')_p]_n \cdot T$  wherein a  $T'$  is covalently bonded to at least one branching agent B in the polymeric product, and wherein p is an integer from 1 to about 10 representing the average number of stable free radical compounds of the formula  $T'$  attached to each branching agent B in the intermediate branched polymeric product, heating a mixture of the intermediate branched polymeric product and at least one second free radical polymerizable monomer of the formula M2 to form a first branched polymeric product of the formula  $A \cdot (M1)_m \cdot [B \cdot (M2)_o \cdot (T')_p]_n \cdot (M2)_o \cdot T$  where o is an integer from 1 to about 5,000 representing the average number of monomers M2 which are inserted between each branching agent B and the stable free radical compounds  $T'$  and T, and cooling the mixture

The resulting product is a branched thermoplastic resin with arms or branches comprised of polymerized monomer with substantially uniform length and narrow polydispersity

The process of the present invention may readily afford telechelic, branched and star polymers having polydispersities of between about 1.1 and 2.0, and at least as low as 1.5 for various polymer systems. Stable free radical polymerization systems of the present invention afford polydispersities that are comparable to those obtained in anionic polymerizations but avoiding the above-described shortcomings and disadvantages of the anionic polymerization processes

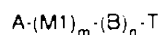
Figure 1 is a schematic representation of an exemplary polymerization and branching sequence in embodiments of the present invention

Figure 2 is a schematic representation of an exemplary polymerization and branching sequence in embodiments of the present invention

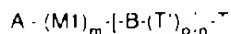
The free radical polymerization process of the present invention may be used to prepare a variety of telechelic, branched and star polymers and copolymers with a variety of molecular architectures in a cost efficient manner. An advantage of the present invention is that the stable free radical polymerization process affords precise control over the molecular architecture of the polymer, including molecular weight, molecular weight distribution, and modality

The present invention provides processes for the preparation of branched thermoplastic resins comprising heating a mixture of a free radical initiator, at least one free radical reactive monomer, at least one free radical reactive branching agent monomer and at least one stable free radical agent, to produce the linear or unbranched polymer product with a free radical initiator fragment at one end and a covalently bonded stable free radical agent at the other end of the polymerized chain of monomers, and irradiating the unbranched polymer product in the presence of a monomer or monomers such as a free radical reactive monomer, a branching agent, and mixtures thereof to form a branched polymeric product. The resulting branched polymeric product can be further elaborated with, for example, chain elongation polymerization, chain branching, and combinations thereof as desired and in accordance with the present invention

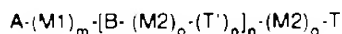
The branched thermoplastic resins may generally be produced in embodiments by the process of heating a mixture comprising an initiator compound of the formula  $A \cdot T$ , wherein A represents a group having at least one carbon atom and is such that a free radical  $A \cdot$  arising therefrom is capable of polymerizing an unsaturated monomer by free radical polymerization and the radical functionality resides on the at least one carbon atom, and T is a covalently bonded stable free radical compound, at least one free radical polymerizable monomer of the formula M1, and at least one free radical reactive branching agent of the formula B, to form an unbranched polymeric product of the formula



where m and n are integers from 1 to about 10,000 representing the total number of monomers M and B contained in the unbranched product, irradiating a mixture of the unbranched polymeric product  $A \cdot (M1)_m \cdot (B)_n \cdot T$  and a second stable free radical compound of the formula  $T'$  to form an intermediate branched polymeric product of the formula

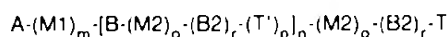


wherein a T' is covalently bonded to at least one branching agent (B)<sub>n</sub> in the polymeric product and where n p is an integer from 1 to about 10 representing the average number of second stable free radical compounds of the formula T' attached to each branching agent B in the intermediate branched polymeric product. Heating a mixture of the intermediate branched polymeric product and at least one second free radical polymerizable monomer of the formula M2 to form a first branched polymeric product of the formula



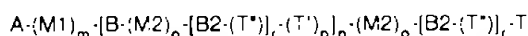
where o is an integer from 1 to about 5 000 representing the total number of monomers M2 which are inserted between each branching agent B and the stable free radical compounds T and T' and cooling the mixture wherein the resulting product is a branched thermoplastic resin with arms or branches comprised of polymerized monomer with substantially uniform length and narrow polydispersity.

Polymerization processes of the present invention can, in embodiments, further comprise the branching sequence of heating the first branched polymeric product with a second branching agent of the formula B2, to form a second intermediate product polymer of the formula



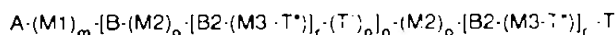
wherein r is an integer from 2 to about 200 and represents the total number of second branching agent monomers B2 which are inserted between each of the covalently bonded stable free radical compounds T and T' and each corresponding branch point.

Irradiating the second intermediate polymer product with at least one third stable free radical compound of the formula T\* to form a branched polymer product of the formula



where T\* is covalently bonded to the branching agents B2 in the resulting polymeric product and

heating the resulting branched polymeric product and at least one third free radical polymerizable monomer of the formula M3 to form a second branched polymer product of the formula



wherein the second branched polymeric product contains at least twice the number of branches as the first branched polymer product.

The aforementioned branching sequence can be repeated numerous times to produce further and more extensive branching of the branched polymer. The branching sequence can be repeated, in embodiments, for example, from 1 to about 20 times.

The branching agent monomers, in embodiments, can contain from 1 to about 10 branching sites and wherein each branching site contains a chromophore which is photolytically active under suitable irradiation, for example, ultraviolet or UV irradiation, whereby upon irradiation a free radical species is generated at substantially each branching site and is subsequently trapped by a stable free radical of the formula such as T' described above. In embodiments, the branching agent monomers contain at least one free radical polymerizable unsaturated double bond and at least one chromophore which is photolytically active when irradiated with a suitable radiation source whereby a free radical species generated therefrom is trapped by a stable free radical agent of the formula such as T' above. When the selected branching agent contains single chromophore which is photolabile, it is referred to as a monofunctional branching agent. Thus, in embodiments, a monofunctional branching agent monomer, in embodiments of the present invention, is incorporated into a polymer chain by, for example, stable free radical mediated polymerization processes and is subsequently selectively photolytically cleaved in the presence additional stable free radical agent to produce a free radical species which is subsequently trapped by the stable free radical agent thereby producing a single branch point. When a plurality of monofunctional branching agents are similarly incorporated into a polymer and thereafter photolyzed and trapped, a substantially equivalent plurality of branch points in the polymer can be established. Likewise, when a

difunctional branching agent is incorporated into a polymer chain and thereafter cleaved and trapped, a bifurcated or double, that is two pronged, branch point is produced. Thus, it is readily understood by one of ordinary skill in the art that the mono-, di-, tri-, and the like, functionality of the branching agent monomer refers to both the number of photochemically cleavable sites and the number of branch points that arise from the branching agent monomer upon photolysis and trapping. A "branch" or "branching point" as used herein refers to a molecular point or loci where subsequent polymer chain extension can be achieved by applying the polymerization and branching sequence of the present invention, and as illustrated herein. Thus, in embodiments of the present invention, a monofunctional branching agent is capable of producing a single branch point and enables a single new polymer chain to be grown or propagated therefrom. A bifunctional branching agent monomer is capable of producing a double branch point and enables two new polymer chains to be grown or propagated therefrom.

Referring to the Figures, there is illustrated in Figure 1 an exemplary polymerization and branching sequence wherein a mixture of a free radical initiator  $I_2$ , such as benzoyl peroxide or azobisisobutyl nitrile, a free radical reactive monomer  $M_1$ , such as styrene or acrylic acid, and a stable free radical agent  $T$ , such as a sterically hindered nitroxide radical compound, are heated to produce the linear or unbranched polymer product  $I-(M_1)_m-T$  where  $m$  is an integer and represents the number of monomers polymerized. In a second step, a monofunctional branching agent  $B$  and the unbranched polymer product are heated to incorporate the branching agent into the polymer product, that is, inserted between the terminal monomer and the stable free radical end group, to form a still unbranched polymer product of the formula  $I-(M_1)_m-(B)_n-T$  where  $n$  is an integer and represents the number of branching agents polymerized or inserted at the end of the polymer chain. Next, the unbranched polymer containing branching agent monomers is irradiated in the presence of a second stable free radical agent  $T'$  to selectively cleave the branching agent so that a free radical species associated with the polymer is generated and thereby creates a branch point, and which free radical species is rapidly trapped by the stable free radical agent  $T'$  to afford a branched polymer product of the formula  $I-(M_1)_m-[B-T']_n-T$ . The branched polymer product is thereafter heated in the presence of a second monomer  $M_2$  which is added to the polymer, or inserted between, at substantially all sites having a covalently bonded stable free radical agent  $-T$  and  $-T'$ , to afford a branched polymer product with polymer chain extensions consisting of  $M_2$  monomers of the formula  $I-(M_1)_m-[B-(M_2)_o-T']_n-(M_2)_n-T$ , wherein  $o$  is an integer and represents the number of  $M_2$  monomers added to, or incorporated within, the branched polymer product; a ratio of  $o/n$  reflects that the total amount of  $M_2$  monomer incorporated into the branched polymer product is substantially equally and uniformly distributed at the chain termini occupied by the covalently bound stable free radical agents,  $-T$  and  $-T'$ . As will be readily evident to one of ordinary skill in the art upon comprehending the teachings of the present invention, when the ratio of  $T/T'$  in the polymer structure is small, for example, when a large amount of branching agent is initially selected, or by way of branching agent selection and subsequent branch elaboration, the amount or relative ratio of  $M_2$  monomer or other added monomers that are incorporated in the polymer chain at  $T$  relative to  $T'$  accordingly is also small.

In Figure 2 there is illustrated an exemplary polymerization and branching sequence wherein a mixture of a free radical initiator  $I_2$ , such as benzoyl peroxide or azobisisobutyl nitrile, only free radical reactive difunctional branching agent monomers  $B$ , and a stable free radical agent  $T$ , are heated to produce the linear or unbranched polymer product  $I-(B)_m-T$ , where  $m$  is an integer and represents the relative number of branching agents polymerized. In a second step, the unbranched polymer product containing branching agent monomers of the formula  $I-(B)_m-T$  is irradiated in the presence of a second stable free radical agent  $T'$  to selectively cleave the difunctional branching agents in the polymer so that a free radical species associated with the polymer are generated and thereby create a plurality of bifurcated or double branch points corresponding to approximately  $2m$ , that is, where there are two free radical species associated with substantially each branching agent site in the polymer, and which free radical species are rapidly trapped by stable free radical agents  $T'$  to afford a branched polymer product of the formula  $I-[B-(T')]_{2m}]_m-T$ . The branched polymer can thereafter be further elaborated in various ways, for example, chain extended by again applying the aforementioned stable free radical mediated polymerization principles, or further branched by applying the branching sequence of the present invention, by heating with one or more free radical reactive monomers  $M_2$ , or a second free radical reactive branching agent  $B_2$ , such that branched polymer of the formulas,  $I-[B-(M_2-T')]_{2m}]_m-(M_2)_n-T$ , and  $I-[B-(B_2-T')]_{2m}]_m-(B_2)_n-T$  respectively, are prepared, wherein  $n$  indicates the relative amount of the last added monomer or branching agent which is inserted between the polymer chain end and the first added stable free radical terminal group  $T$ .

In other embodiments of the present, it is possible to copolymerize mixtures of mono- and or difunctional free radical reactive monomers, such as olefins and dienes, with mono- or multifunctional branching agent monomers to produce various branched copolymer architectures or copolymeric segments structures which contain both monomer types. Some advantages of the aforescribed process variant include the ability to prepare highly branched copolymeric materials, and the ability to eliminate additional, separate, or unnecessary polymerization and branch point introducing reaction steps.

Any suitable branching agent can be selected so long as the objectives of the present invention are achieved. As used herein "branching agent" refers to two related but functionally different compound classes. Each branching agent

class provides an operator with unique molecular design flexibility and control over the polymer chain length and level of branching which can be achieved in a selected branching polymerization process or combined chain elongation and branching sequence

One class of branching agent referred to in embodiments as a "branching agent monomer" comprises compounds which are capable of sequentially undergoing or performing both thermal polymerization with a free radical species that is, polymer chain propagation and integration into a growing polymer chain, and thereafter undergoing photochemically induced branch point formation. A branching agent monomer compound of the present invention has at least one free radical reactive and therefore polymerizable double bond, and at least one chromophore which can be selectively photochemically activated to enable the formation of at least one free radical specie which can be trapped by the presence of either a stable free radical compound, such as T<sup>•</sup>, which leads to a reversibly terminated branch site or a second free radical reactive monomer compound which leads to uncontrolled free radical polymerization and chain elongation in the absence of excess stable free radical trapping agent

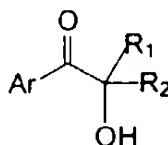
Another class of branching agent useful in the present invention, also referred to in embodiments as an "inhibiting branching agent", comprises compounds which are capable of sequentially inhibiting thermal polymerization, that is polymer chain termination, and thereafter undergoing photochemically induced branch point formation. Thus, an "inhibiting branching agent" has a first function to inhibit or terminate initial polymer chain extension by terminating or irreversibly blocking further monomer addition by reacting with the propagating free radical species and a second function to selectively allow branch point formation by of appropriate selective photochemical cleavage

An important distinction between the aforementioned branching agent monomer compounds and an inhibiting branching agent compounds is that the branching agent monomers by definition and design provide for polymer chain propagation at branch point loci as well as polymer chain propagation at the predecessor polymer chain, that is the polymer chain which originally incorporated the branching agent. The inhibiting branching agent compounds provide for polymer chain propagation only at branch point loci and substantially limit or preclude chain propagation of the predecessor polymer chain

In embodiments of the present invention, branching agent monomer compounds and inhibiting branching agent compounds, are preferably used separately in separate branching schemes, however they can be used together in admixtures if desired and with the understanding that the presence of the inhibiting branching agent can lead to slow reactions and long reaction periods

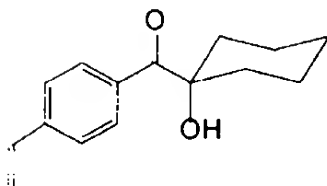
In embodiments, preferred branching agent monomer compounds are, for example, olefin containing dialkyl substituted alpha hydroxy aryl ketones, wherein the olefin provides for the aforementioned predecessor polymer chain elongation, and the hydroxy aryl ketone functional grouping provides the chromophore for photochemical activation and cleavage leading to the formation of the branch point. Other example classes of branching agent monomers include b,s-dialkyl substituted alpha hydroxy aryl ketones and still other example classes include those described by S. P Pappas "Photoinitiated Polymerization" in Comprehensive Polymer Chemistry, The Synthesis and Characterization, Reactions and Applications of Polymers, Volume 4, Pergamon Press, Oxford. These compounds can be readily functionally modified for use in the present invention by attaching a polymerizable group, such as a vinyl group, to the photoinitiator portion of the molecule. Furthermore, olefin containing acylphosphine oxides, of the general structure R<sub>1</sub>C(O)-P(O)R<sub>2</sub>R<sub>3</sub>, where at least one R group contains a polymerizable double bond, and which compounds undergo a Norris Type I cleavage, also function as suitable branching agents in pseudoliving polymerization

Suitable monofunctional branching agent monomer compounds B can be of the general formula

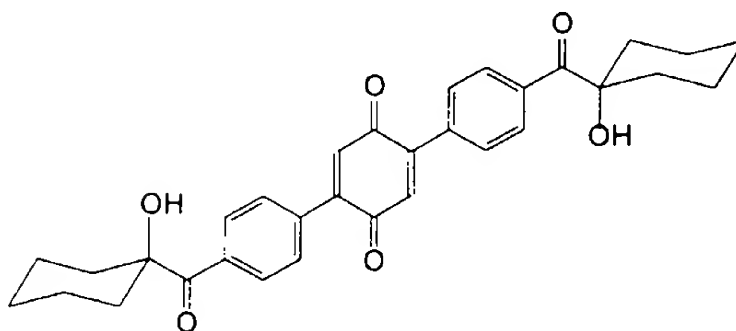


wherein Ar is an aryl group containing at least one free radical polymerizable unsaturated double bond and from 8 to about 26 carbon atoms, and R<sub>1</sub> and R<sub>2</sub> are independently selected from the group consisting of alkyl, alkylene, alkylaryl, and cycloalkyl substituents with from 1 to about 20 carbon atoms

An exemplary branching agent monomer compound B is of the formula



An exemplary inhibiting branching agent compound B is the disubstituted quinone compound of the formula



wherein the quinone portion of the molecule provides free radical chain polymerization inhibition and the hydroxy aryl ketone moieties provide the latent or masked photochemically activated branching sites

In embodiments, processes of the present invention can further comprise combining the branched resin with, for example, a thermoplastic resin, a colorant, a charge control additive, a surfactant, an emulsifier, a pigment dispersant, and mixtures thereof to form a subsequent mixture which can be further melt blended in a suitable melt mixing apparatus to form a toner suitable for use in xerographic and related marking applications

In embodiments of the present invention, the initiator compound  $I_2$  or A-T can have a half life of about 5 seconds to about 5 minutes at a temperature from about 80°C to about 180°C.

Polymerizable monomers suitable for use in the present invention, in embodiments, include any free radical reactive unsaturated compounds such as styrenes, conjugated dienes, acrylate esters and alkyl acrylate esters with from 5 to 25 carbon atoms, N-vinyl acetates, amine, carboxyl, aldehyde, alkyl, cyano, and hydroxyl substituted acrylic acids and acrylic acid esters having from 2 to about 20 carbon atoms, acrylamide, methacrylamide, acrylic acid, methacrylic acid, acrolein, dimethylaminoacrylate, hydroxy-lower alkyl, and amino-lower alkyl acrylates of the formula  $CH_2=C(R^1)(C-Z)-R^2$  where  $R^1$  is hydrogen,  $R^2$  is selected from the group consisting of  $-OR^3$  and  $-NR^3_2$ , and wherein Z is selected from the group consisting of oxygen and sulfur atoms. In embodiments, from 1 to about 10 different free radical polymerizable monomers can be selected and simultaneously polymerized in any one monomer addition polymerization step

In embodiments of the present invention, the polydispersity of the arms or branches is narrow and generally is from about 1.0 to about 1.7, while the monomer to polymer conversions typically range of from about 10 to about 100 percent depending upon polymerization and branching conditions selected, the extent to which the steps in the branching process are completed, and the number of times the branching sequence is successively repeated

The heating conditions selected for accomplishing the stable free radical mediated monomer addition polymerization can be for a period of time of from about 30 minutes to about 60 hours and at a temperature of from about 70 to about 250°C. Upon completion of a monomer addition polymerization into the chain ends, the reaction mixture is preferably cooled to below about 80 to 100°C, and preferably below about 40°C to temporarily or permanently suspend the monomer addition polymerization process

The weight average molecular weight ( $M_w$ ) of the resulting arms or branches which have been appended to the branch points are, for example, independently from about 2,000 to about 200,000 and depend upon the conditions selected and the extent of repetition of the branching sequence

The present invention provides stable free radical mediated polymerization processes for preparing branched polymers such as dendrimeric thermoplastic resins or elastomeric materials with well defined molecular structure, molecular weight properties, and narrow polydispersities. The processes can be run as batch, semi-continuous, continuous processes, or combinations thereof. The processes can be carried out in solution, bulk, suspension, emulsion, phase transfer, and extrusion reaction conditions. The processes provide for from about 1 to about 99 percent by weight



of the reaction mixture to be a free radical reactive monomer or monomer mixtures and the thermally controlled chain elongation polymerization processes can be conducted at from about 100°C to about 250°C. The processes produce branched polymer products which have operator selectable low, intermediate, or high molecular weight, well defined branching properties including the branching number and the extent of branching, narrow polydispersity, low residual salt content or are salt free, and can have low toxicity.

Suitable stable free radical compounds for use in the present are known, and can be prepared prior to mixing with the other polymerization reactants or they may be generated in situ or on an as needed basis.

The stable free radical agent compounds of the present invention may be generated in any suitable fashion from the corresponding non-free radical precursor, for example, thermally, chemically, electrochemically, photolytically, mechanically, and the like methods.

Examples of suitable and preferred stable free radicals are disclosed in U.S. Patent No. 3,600,169.

The stable free radical compound when covalently bound to the branched polymer product preferably has no unpaired electrons, that is, has no free radical character or free unpaired electrons.

Suitable initiators for the branching polymerization processes of the present invention are any conventional free radical initiators which have a half-life of at least 1 second at the polymerization temperature. Preferably, the initiator will have a half life of from about 10 second to about 2 hours, more preferably from about 10 seconds to about 10 minutes at the polymerization reaction temperature. These initiators include, but are not limited to oxygen, hydrogen peroxide, certain alkyl hydroperoxides, dialkyl peroxides, peresters, percarbonates, peroxides, persulfates and azo initiators. The initiators are normally used in amounts of from about 0.05 percent to about 33 percent based on the weight of total polymerizable monomer. A preferred range is from about 0.5 to about 20 percent by weight of the total polymerizable monomer. In embodiments, the molar ratio of monomer to stable free radical agent to free radical initiator compounds, such as I<sub>2</sub> or A-T, is from about 1:0.02:1.0 to about 20,000:2.5:1.0. Preferred free radical initiators do not react with or degrade the stable free radical compounds with the exception of the aforementioned in situ stable free radical generation resulting from the reaction of the stable free radical precursor compound with a free radical fragments species.

In other embodiments, the polymerization processes of the present invention can be used to prepare branched block copolymers and multi-block polymers having narrow polydispersity properties wherein at least one of the blocks is optionally water soluble thereby providing, for example, a means for preparing branched surface active agents or surfactant materials having well defined polydispersity and hydrophobe-lipophile balance (HLB) properties.

Described herein are hydrocarbon star polymers prepared by a stable free radical mediated free radical polymerization process in which precise control over the length of the star side chains is maintained. This control provides substantial advantages in the applications of viscosity modification, matrix strengthening and thermoplastic clarity improvement since these properties depend to a substantial extent on the tertiary structure of the star polymer.

The dendrimers can be selected as toner additives, for example, as illustrated in the documents mentioned herein. Dendrimers are known and can be considered radially symmetrical molecules of a STARBURST™ topology comprised of an initiator core, such as nitrogen, ethylenediamine, silicon, and the like, interior layers attached to the core and comprised of, for example, three, four or more arms, each arm being composed of repeating units with the number of repeating units in each arm being considered the generation of the dendrimer, and terminal covalently bonded stable free radical functional groups, such as a nitroxyl compound attached to the outermost generation, which dendrimers having related terminal amine terminated groups are illustrated, for example, in U.S. Patent 4,587,329 and in *Angewandte Chemie, Int. Ed. Engl.*, 29, 138 (1990). The synthesis of dendrimers usually occurs by a linear, convergent, or divergent approaches. An alternate synthetic route uses a convergent growth synthesis as described in detail in C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 112, 7638 (1990).

Although not desired to be limited by theory, it is believed that photoinitiation or photolysis of the branching agent compound or compounds produce free radical species, generally by a Norrish Type I mechanism. The resulting radicals initiate polymerization of available free radical reactive monomer(s) molecules. However, since a stable free radical such as TEMPO is present, either the low molecular weight photoinitiator fragment, or the contiguous polymer fragment, such as a short oligomer chain, are captured by excess stable free radical, to afford for example a TEMPO-polymer intermediate product. On thermolysis, the TEMPO-polymer bond ruptures to produce a radical species on the polymer chain end which subsequently captures additional monomer thereby providing a pseudoliving polymerization reaction mechanism. Any low molecular weight photoinitiator fragment-TEMPO by product can be readily separated from the higher molecular weight branched polymeric product by various known methods, for example, solvent precipitation, extraction, or washing.

The branching polymerization reactions of the present invention can be accomplished in the absence of solvents or supplemented with a solvent or cosolvent if desired to help ensure that the reaction mixture or at least the monomer containing portion remains a homogeneous single phase throughout the monomer conversion. Any solvent or cosolvent may be selected so long as the solvent media is effective in providing a solvent system which avoids precipitation or phase separation of the reactants or polymer products until after all the solution polymerization reactions have been

completed

The molecular weights referred to are measured by gel permeation chromatography using, for example, a polyethylene oxide standards for water soluble polymers and polystyrene standards for organic soluble polymers unless specifically stated otherwise

During the reaction of monomer or mixtures of monomers to form polymers, the reaction time may be varied over about 30 minutes to 60 hours, preferably between about 2 to 10 hours and optimally about 3 to 7 hours. The optimal reaction time may vary depending upon the temperature, the volume and scale of the reaction, the extent and degree of branching, and the quantity and type of polymerization initiator and stable free radical agent selected.

Irradiation can be accomplished by conventional means using, for example, a conventional ultraviolet source - quartz reactor and suitable equivalents.

The molar ratio of the stable free radical (SFR) agent to free radical initiator (INIT) residing in the monomer phase can, in embodiments, be from about 0.5 to about 5.0 and preferably in the range from about 0.4 to 4.0. Although not wanting to be limited by theory, in an embodiment, the molar ratio (SFR/INIT) of stable free radical agent, for example, 2,4,6-tri-tert-butyl phenoxy radical, to free radical initiator, for example, benzoyl peroxide is about 2.0 and is believed to be important for success of the process. If the [SFR/INIT] is too high then the reaction rate is noticeably inhibited. If the [SFR/INIT] is too low then the reaction product has undesired increased polydispersity.

In embodiments, the molar ratio of monomer content to stable free radical agent to free radical initiator is from about 6.0:0.2:1 to about 10.0:0.2:5.1 and preferably in the range of about 1.25:2.0:1 to about 7.0:0.1:3.1, for example, as used in preparing the aforementioned polymeric branching agents.

The amount of branching agent used in the polymerization process, specifically chain elongation or branching steps depends upon the extent of chain elongation and branching desired in the resulting polymer. In embodiments of the present invention, the molar ratio of monomer to branching agent can be in the range of from about 100:0.1 to about 0.1:100. However, it should be emphasized that the above ratios for branching agent correspond to representative and not limiting amounts and the ratios of such compounds that can be present in the reactor vessel upon commencing the stable free radical polymerization process. Other suitable ratios of monomer to branching agent include, 0.0:100, that is, where no monomer is selected and only branching agent is polymerized as illustrated in Figure 2, particularly in path ii), and 100:0.0, that is, where no branching agent is selected, for example, in those process steps where chain elongation with monomer only is the desired result, as for example illustrated in path I) of the Figure. The present invention, in embodiments, comprises polymerization processes which include at least one branch point introduction and formation step, and optionally at least one branch point chain elongation step.

Additionally, the polymerization reaction rate of the monomer or monomers may, in embodiments of the present invention, be accelerated and the reaction time reduced by the addition of a catalyst. For example, a catalytic amount of a protic acid, which will not also initiate cationic polymerization, may be added to the reaction mixture.

In embodiments, the thermoplastic resin polymers of the present invention are preferably polymerized in an inert atmosphere, that is, with the virtual exclusion of oxygen. Embodiments of the present invention therefore conduct the stable free radical polymerization process in an inert atmosphere, such as under an argon or nitrogen blanket.

A further discussion of reaction conditions and reactants, including suitable monomers, stable free radical agents, catalysts, etc. may be found in U.S. Patent No. 5,322,912.

Following completion or termination of the reaction, the resultant polymer and/or by product oligomers can be optionally separated from the reaction mixture, and washed and dried. Subsequent processing of the thermoplastic resin polymer can then be conducted.

Alternatively, branched block copolymer resins may also be prepared whereby after each desired block has been formed a new monomer or monomers is added, without the addition of more initiator or stable free radical agent, to form a new block wherein each block component is well defined in length and has a narrow molecular weight distribution and having properties depending on the repeated sequence and the monomers chosen for incorporation. Monomers added subsequent to the formation of the first formed branched thermoplastic resin or elastomer may be water soluble or water insoluble. Judicious selection of the water solubility properties of added monomers and the resulting polymeric segment enables convenient synthetic routes to branched block and multiblock copolymers with narrow polydispersities that are useful, for example, as surfactants, resin compatibilizers, such as "molecular velcro" and the like, viscosity modifiers, emulsifiers, and the like.

The branched polymeric products of the present invention may be optionally crosslinked with, for example, known crosslinking, coupling or curing agents such as divinyl benzene and the like, either in situ or in a separate post polymerization process step.

Additional optional known additives may be used in the polymerization reactions which do not interfere with the objects of the invention and which may provide additional performance enhancements to the resulting branched product, for example, colorants, lubricants, release or transfer agents, surfactants, stabilizers, antifoams, antioxidants, and the like.

Polymer resins possessing a discrete mixture of monomodal, that is a well defined multimodal molecular weight

distribution may in embodiments thereof provide several advantages, particularly for electrophotographic toner compositions such as melt rheology properties including improved flow and elasticity and improved performance properties such as triboelectrification, admix rates, and shelf life stabilities.

The invention will further be illustrated in the following non limiting Examples. Parts and percentages are by weight unless otherwise indicated.

## EXAMPLES

**A-T PHOTOINITIATOR PREPARATION** Photoinitiator 1-hydroxycyclohexyl phenyl ketone ( 1.06 g ) and TEMPO ( 2.06 g ) were dissolved in heptane (30 mL without prior deoxygenation) and subjected to UV irradiation. The light source used was a high pressure 450 W Hanovia mercury vapor lamp which was placed in a water cooled quartz immersion well (Ace Glass Co.). The immersion well was placed in a 2 liter beaker containing water and the reaction sample containing the reagents in heptane was placed in the beaker in a long glass Craig tube. After 17.5 hours of irradiation, the sample was placed in a separatory funnel and extracted with a water-methanol mixture 1:1 v/v, 4 times at 50 mL each, to remove the excess TEMPO and the remaining heptane solution (6.0 g) and the resulting compound A-T was used directly in the next step.

**LIVING POLYMERIZATION** The initiator A-T ( 6.0 g ) was added to a mixture of sodium styrene sulfonate ( 15 g ), ethylene glycol ( 24 g ) and water ( 16 g ) and heated to 110 °C. Alternatively, the mixture could be photolyzed to initiate polymerization. After 3 hours, ferrous sulfate heptahydrate ( about 50 mg ) was added to reduce any excess TEMPO which had not been removed during the aforementioned extraction procedure. Heating was continued for 18 hours. During this time, four aliquots of the reaction mixture were removed and gel permeation chromatograms (GPC) recorded. The GPC results indicated that the polymerization was living and that the baseline is free of any traces of dead or terminated polymer.

Table 1 shows the molecular weight change as a function of reaction aliquot. The narrowing polydispersity further supports the living nature of this polymerization.

Table 1

SAMPLE	M <sub>n</sub>	M <sub>w</sub>	M <sub>p</sub>	PD
1	40,491	59,224	59,024	1.453
2	60,696	100,857	104,955	1.662
3	15,974	22,862	21,053	1.431
4	68,540	139,727	133,296	1.578

**A-T PHOTOINITIATOR PREPARATION CONTAINING BRANCHING AGENT** Photoinitiator 1-hydroxycyclohexyl 4-vinyl phenyl ketone ( 1.20 g ) and TEMPO ( 2.06 g ) are dissolved in heptane (30 mL without prior deoxygenation) and subjected to UV irradiation. The light source used is a high pressure 450 W Hanovia mercury vapor lamp, which is placed in a water cooled, quartz, immersion well (Ace Glass Co.). The immersion well is placed in a 2 liter beaker containing water and the reaction sample containing the reagents in heptane is placed in the beaker in a long glass tube. After 17.5 hours of irradiation, the sample is placed in a separatory funnel and extracted with a water-methanol mixture 1:1 v/v, 4 times at 50 mL each, to remove the excess TEMPO and the remaining heptane solution (6.0 g) and the resulting compound A-T is used directly for chain extension or branching.

## EXAMPLE I

**PREPARATION OF BRANCHED POLYMERS** For branched polymers, various amounts of a co-monomer containing a photolyzable or photolabile group, such as the aforementioned alpha hydroxy ketones, is incorporated into the backbone of the polymer or oligomer. On cooling to room temperature and photolysis in the presence of a stable free radical compound such as TEMPO, each photolyzable group of the covalently bound branching agent becomes a TEMPO terminated branch point capable of thermally induced stable free radical cleavage and subsequent stable free radical mediated monomer polymerization and narrow polydispersity chain growth. Byproducts such as monomeric TEMPO terminated photolysis products can be readily removed from the polymer so that no new chains grow as a result of their photolysis and propagation.

**EXAMPLE II**

**PREPARATION OF STAR POLYMERS** For the preparation of star polymers, a small amount of an initiator compound A-T containing a photolyzable group, such as the aforementioned disubstituted quinone compound, is incorporated into the polymer chain backbone by thermally controlled copolymerization with monomers. On cooling, for example, to room temperature and photolysis, and in the presence of TEMPO or similar stable free radical compound, each photolyzable group becomes a TEMPO terminated star point which is capable of subsequent to thermal or photochemical induced stable free radical living polymerization processes. The process of sequential chain growth or elongation and chain branching, can be repeated many times to provide dendritic structures.

**EXAMPLE III**

**MAGNETIC TONER PREPARATION AND EVALUATION** The polymer resin (74 weight percent of the total mixture) obtained by the stable free radical polymerization processes described in Example II may be melt extruded with 10 weight percent of REGAL 330® carbon black and 16 weight percent of MAPICO BLACK® magnetite at 120°C, and the extrudate pulverized in a Waring blender and jetted to 8 micron number average sized particles. A positively charging magnetic toner may be prepared by surface treating the jetted toner (2 grams) with 0.12 gram of a 1:1 weight ratio of AEROSIL R972® (Degussa) and TP-302 a naphthalene sulfonate and quaternary ammonium salt (Nachem/Hodogaya SI) charge control agent.

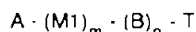
Developer compositions may then be prepared by admixing 3.34 parts by weight of the aforementioned toner composition with 96.66 parts by weight of a carrier comprised of a steel core with a polymer mixture thereover containing 70 percent by weight of KYNAR®, a polyvinylidene fluoride, and 30 percent by weight of polymethyl methacrylate, the coating weight being about 0.9 percent.

Toner compositions may be readily prepared by conventional means from the branched polymer and copolymer resins of the present invention including colored toners, single component toners, multi-component toners, toners containing special performance additives, and the like.

The branched polymers and copolymers of the present invention find utility in a wide variety of applications such as the improvement of the rheological properties of thermoplastic resins by blending in polystyrene star polymers, improving the compatibility of polymer blend by adding small amounts of the branched polymers as compatilizing agents, improving the viscosity index of lubricating oils, the use of these materials as a dispersant and improving the impact strength of polyphenylene ether resins. The branched polymeric products of the present invention may contain various polymeric segments such as homopolymers, random copolymers, diblock copolymers, multiblock copolymers, tapered copolymers, and combinations thereof.

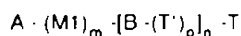
**Claims**

1. A process for the preparation of branched thermoplastic resins comprising heating a mixture comprising an initiator compound of the formula A-T, wherein A represents a group having at least one carbon atom and is such that a free radical A· arising therefrom is capable of polymerizing an unsaturated monomer by free radical polymerization and the radical functionality resides on at least one carbon atom, and T is a covalently bonded stable free radical compound, at least one free radical polymerizable monomer of the formula M1, and at least one free radical reactive branching agent of the formula B, to form an unbranched polymeric product of the formula



where m and n are integers from 1 to about 10,000 representing the total number of monomers M and B contained in the unbranched product.

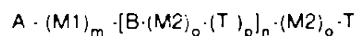
irradiating a mixture of the unbranched polymeric product and a second stable free radical compound of the formula T'· to form an intermediate branched polymeric product of the formula



wherein a T'· becomes covalently bonded to at least one branching agent B in the polymeric product, and wherein p is an integer from 1 to about 10 representing the average number of stable free radical compounds of the formula

T' attached to each branching agent B in the intermediate branched polymeric product.

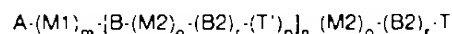
heating a mixture of the intermediate branched polymeric product and at least one second free radical polymerizable monomer of the formula M2 to form a first branched polymeric product of the formula



where o is an integer from 1 to about 5 000 representing the average number of monomers M2 which are inserted between each of the covalently bonded stable free radical compounds T and T' and each branch point, and

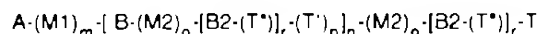
cooling the mixture

2. A process in accordance with claim 1, further comprising the further branching steps of heating the first branched polymeric product with a second branching agent of the formula B2 to form a second intermediate product polymer.



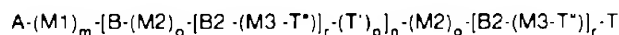
wherein r is an integer from 2 to about 200 and represents the total number second branching agent monomers B2 which are inserted between each of the covalently bonded stable free radical compounds T and T' and each branch point.

irradiating the second intermediate polymer product with at least one third stable free radical compound of the formula T\* to form a branched polymer product of the formula



where T\* is covalently bonded to the branching agents B2 in the resulting polymeric product.

heating the resulting branched polymeric product and at least one third free radical polymerizable monomer of the formula M3 to form a second branched polymer product of the formula

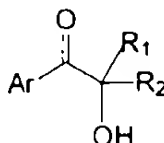


wherein the second branched polymeric product contains at least twice the number of branches as the first branched polymer product and

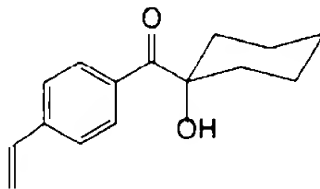
optionally repeating said further branching steps from 1 to about 20 times

3. A process in accordance with either of claims 1 or 2, wherein said branching agent B contains from 1 to about 10 branching sites and wherein each branching site contains a chromophore which is photolytically active under irradiation whereby upon irradiation, a free radical species is generated at substantially each branching site and is subsequently and rapidly trapped by a stable free radical agent compound
4. A process in accordance with claim 3 wherein the branching agent B contains at least one free radical polymerizable unsaturated double bond
5. A process in accordance with any of claims 1 to 4 wherein the branching agent B is selected from the group consisting of

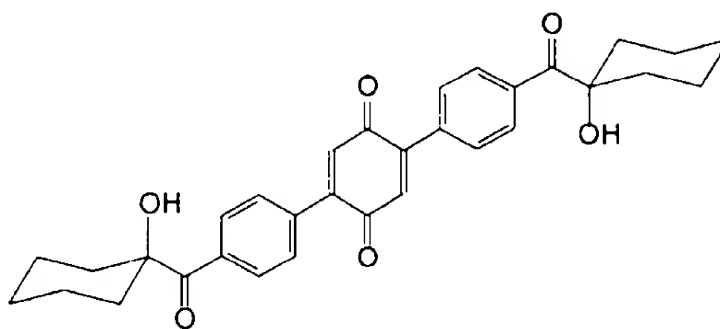
(a) a branching agent monomer compound of the formula



wherein Ar is an aryl group containing at least one free radical polymerizable unsaturated double bond and from 8 to about 26 carbon atoms and  $R_1$  and  $R_2$  are independently selected from the group consisting of alkyl, alkylene, alkylaryl, and cycloalkyl substituents with from 1 to about 20 carbon atoms  
 (b) a branching agent monomer which is photolytically monofunctional of the formula



(c) an inhibiting photolytically difunctional compound and is of the formula



and any mixtures thereof

6. A process in accordance with any of claims 1 to 5, wherein the initiator compound A-T has a half life of about 5 seconds to about 5 minutes at a temperature from about 80°C to about 180°C
7. A process in accordance with any of claims 1 to 6, further comprising combining the formed resin product with at least one member selected from the group consisting of a thermoplastic resin, a colorant, a charge control additive, a surfactant, an emulsifier, and a pigment dispersant, to form a toner mixture, and wherein the mixture is further melt blended to form a melt blended toner
8. A process for the preparation of branched thermoplastic resins comprising

heating a mixture of a free radical initiator  $I_2$ , at least one free radical reactive monomer M1, and a stable free radical agent T, to produce the linear or unbranched polymer product of the formula  $I-(M1)_m-T$ , where m is an integer and represents the number of monomers polymerized  
 heating separately or sequentially at least one monofunctional branching agent B and the unbranched polymer product to form a second unbranched polymer product of the formula  $I-(M1)_m-(B)_n-T$ , where n is an integer and represents the number of branching agents polymerized or inserted at the end of the polymer chain  
 irradiating the second unbranched polymer in the presence of a second stable free radical agent T' to afford a branched polymer product of the formula  $I-(M1)_m-(B-T')_n-T$ , and  
 heating the branched polymer product with a second monomer, to afford a first branched polymer of the formula  $I-(M1)_m-(B-(M2)_o-T')_n-(M2)_o-T$ , wherein o is an integer and represents the total number of M2 monomers incorporated into the first branched polymer product

9. A process for the preparation of branched thermoplastic resins comprising heating a mixture of a free radical initiator  $I_2$ , at least one difunctional free radical reactive branching agent monomer B, and a stable free radical agent T, to produce the linear or unbranched polymer product of the formula  $I-(B)_m-T$ , where m is an integer and represents the number of branching agents polymerized, and

irradiating the unbranched polymer product in the presence of a second stable free radical agent T' to form a branched polymer product of the formula  $I-[B-(T')_2m]_n-T$

- 5 10. A process for the preparation of branched thermoplastic resins comprising heating a mixture of a free radical initiator, at least one free radical reactive monomer, at least one free radical reactive branching agent monomer, and at least one stable free radical agent to produce a linear or unbranched polymer product with a free radical initiator fragment at one end and a covalently bonded stable free radical agent at the other end of the polymerized chain of monomers, and irradiating the unbranched polymer product in the presence of a monomer or monomers selected from the group consisting of a free radical reactive monomer, a branching agent, and mixtures thereof to form a branched polymeric product
- 10

15

20

25

30

35

40

45

50

55

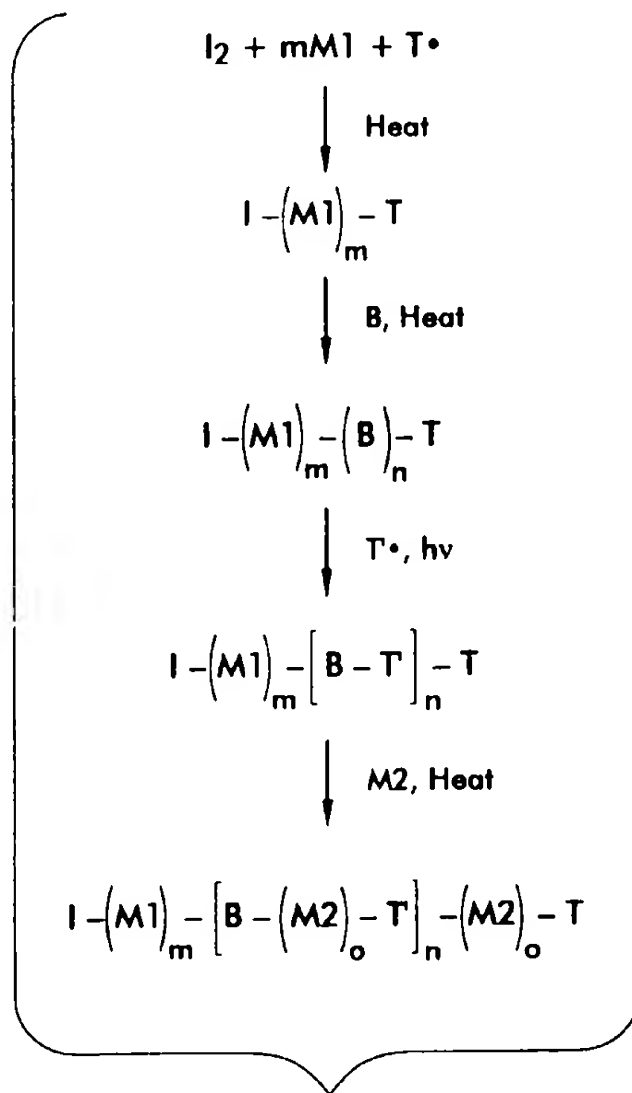


FIG. 1



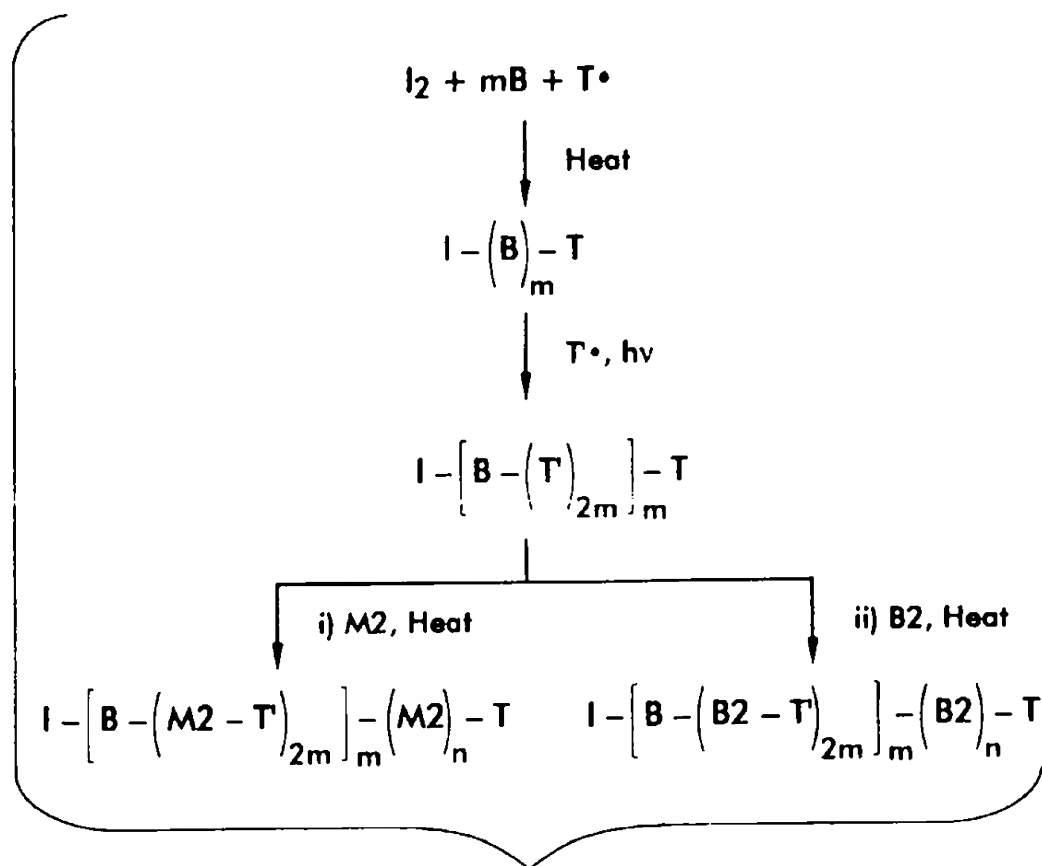
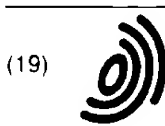


FIG. 2



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 814 097 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3  
06.05.1999 Bulletin 1999/18

(51) Int Cl<sup>6</sup> C08F 4/00, C08F 293/00,  
C08F 291/00

(43) Date of publication A2  
29.12.1997 Bulletin 1997/52

(21) Application number 97303948.0

(22) Date of filing 06.06.1997

(84) Designated Contracting States  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

(30) Priority 17.06.1996 US 664702

(71) Applicant XEROX CORPORATION  
Rochester, New York 14644 (US)

(72) Inventors  
• Kazmaier, Peter M.  
Mississauga, Ontario L5L 1E5 (CA)  
• Keoshkerian, Barkev  
Thornhill, Ontario L4J 7E8 (CA)

• Moffat, Karen A.  
Brantford, Ontario N3P 1N2 (CA)  
• Georges, Michael K.  
Guelph, Ontario N1G 3N8 (CA)  
• Hamer, Gordon K.  
Mississauga, Ontario L5L 2P4 (CA)  
• Veregin, Richard P.N.  
Mississauga, Ontario L5L 5C3 (CA)

(74) Representative Pike, Christopher Gerard et al  
Rank Xerox Ltd.,  
Patent Department,  
Parkway  
Marlow, Buckinghamshire SL7 1YL (GB)

(54) Processes for preparing telechelic, branched and star thermoplastic resin polymers

(57) A process for the preparation of branched thermoplastic resins comprising heating a mixture of a free radical initiator at least one first free radical reactive monomer at least one free radical reactive branching agent compound, and at least one stable free radical agent, to produce a linear or unbranched polymer product with a free radical initiator fragment at one end and

a covalently bonded stable free radical agent at the other end of the polymerized chain of monomers, and irradiating the unbranched polymer product in the presence of a reactive compound selected from the group consisting of a free radical reactive monomer a branching agent compound, and mixtures thereof to form a branched polymeric product

EP 0 814 097 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 3948

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication where appropriate of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.6)
P, X	EP 0 735 064 A (XEROX CORP) 2 October 1996	1, 3, 4, 6, 7, 10	C08F4/00 C08F293/00 C08F291/00
Y	* claim 37, page 7, line 16-17, claims 35, 36, 38, claims 12, 13, claims 1, 11, page 6, line 35 - page 7, line 21, page 9, line 13-34, page 10, line 18, 58 * * page 12, line 46 - page 13, line 25 *	5	
D, Y	S.P. PAPPAS: "PHOTOINITIATED POLYMERISATION" IN COMPREHENSIVE POLYMER CHEMISTRY, THE SYNTHESIS AND CHARACTERISATION, REACTIONS AND APPLICATIONS OF POLYMERS, VOLUME 4, PERGAMON PRESS, OXFORD XP002094485 * page 339, formulas 3, 4 *	5	
A	US 5 498 679 A (MOFFAT KAREN A ET AL) 12 March 1996 * the whole document *	1-10	
A	WO 94 11412 A (XEROX CORP) 26 May 1994 * page 7, line 1-21 *	1-10	TECHNICAL FIELDS SEARCHED (Int Cl.6) C08F G03G
D, A	EP 0 349 270 A (MINNESOTA MINING & MFG) 3 January 1990 * claims 4, 10 * * page 3, line 13 - page 5, line 18 *	1-10	

The present search report has been drawn up for all claims

Place of search

THE HAGUE

Date of completion of the search

24 February 1999

Examiner

Hammond, A

### CATEGORY OF CITED DOCUMENTS

- X particularly relevant: taken alone
- Y particularly relevant: combined with another document of the same category
- A technological background
- C non-written disclosure
- P intermediate document

- T theory or principle underlying the invention
- E earlier patent document, but published only after the filing date
- D document cited in the application
- L document cited for other reasons
- S member of the same patent family, corresponding document

EP 0 814 097 A3

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 30 3948

This annex lists the patent family members relating to the patent documents cited in the above mentioned European search report.  
The members are as contained in the European Patent Office EPO file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-02-1999

Patent document cited in search report		Publication date	Patent family members:	Publication date
EP 0735064	A	02-10-1996	US 5773510 A	30-06-1998
			CA 2173006 A	01-10-1996
			JP 8269106 A	15-10-1996
US 5498679	A	12-03-1996	NONE	
WO 9411412	A	26-05-1994	US 5322912 A	21-06-1994
			AU 5295593 A	08-06-1994
			BR 9305751 A	28-01-1997
			CA 2126670 A,C	26-05-1994
			CN 1087349 A	01-06-1994
			EP 0621878 A	02-11-1994
			JP 6199916 A	19-07-1994
			MX 9307085 A	30-06-1994
			US 5401804 A	28-03-1995
			US 5549998 A	27-08-1996
EP 0349270	A	03-01-1990	AU 614140 B	22-08-1991
			AU 3523989 A	04-01-1990
			DE 68917657 D	29-09-1994
			DE 68917657 T	23-03-1995
			ES 2057127 T	16-10-1994
			JP 2103277 A	16-04-1990
			MX 169747 B	22-07-1993

EPO: 08/04/1999

For more details about this annex see Official Journal of the European Patent Office No. 12/82